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Chemical Modification of Lignin-Rich Paper
Part 9: Effect of Dry Heat and Moist Heat on the Accelerated Yellowing of Untreated and Acetylated High-Yield Pulps

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Chemical modification of lignin-rich paper

Part 9. Effect of dry heat and moist heat on the accelerated yellowing of untreated and acetylated high-yield pulps

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SUMMARY: The effect of two different aging conditions (e.g., 105°C and 80°C, 65% relative humidity) on the heat-induced yellowing of dithionite-bleached and hydrogen-peroxide-bleached spruce thermomechanical pulp (TMP) and hydrogen-peroxide-bleached spruce and aspen chemithermomechanical pulp (CTMP) has been examined.

The heat-induced discoloration of the bleached pulps was found to proceed in more or less two phases, i.e., an initial phase with a large drop in brightness followed by a slower phase. The phases were, however, not so well-marked during heat-induced aging as during light-induced discoloration. The most heat-resistant pulp was the aspen CTMP followed by the hydrogen-peroxide-bleached spruce TMP. The spruce CTMP and the dithionite-bleached spruce TMP were the least stable, although the difference between the softwood pulps was small.

Acetylation was found to improve strongly the heat-induced stability of all of the pulps examined even at a low extent of derivatization. These results together with earlier findings, showing that a low degree of acetylation substantially increases the photostability of different types of high-yield pulps and that the order of discoloration under different light sources was approximately the same for the pulps examined in this work, suggest that light-induced and heat-induced yellowing possibly involves very similar reaction pathways in the lignin moiety. The participation of the pulp carbohydrates could, however, not be excluded because the carbohydrates most likely, to some degree, are also derivatized, even at low acetyl levels.

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The loss of brightness, often referred to as yellowing, which occurs when lignin-rich paper is exposed to light or heat, is the main hindrance to the more widespread use of high-yield pulps in high-quality and long-life paper grades (such as writing, archive, and publication paper). The world production capacity of mechanical pulps is today about 38.2 million tons per year (Barnet 1997), a figure that would increase considerably if the brightness stability could be improved (Cockram 1989; Ford, Sharman 1996).

Brightness reversion of high-yield pulps may be caused by light or heat. Many studies have shown that the light-induced discoloration is the most damaging and is mainly caused by several complex reactions of the lignin present in the pulp (cf. Heitner, Schmidt 1991; Leary 1994). Different opinions have been expressed about the mechanism for the heat-induced discoloration. Several research groups have suggested that the thermal reversion and photoreversion involve very similar reactions in the lignin moiety (Gellerstedt, Pettersson 1980; Gellerstedt et al. 1983; Gratzl 1985; Chong et al. 1990). Other research groups have, however, reported that color reversion induced by heat and by light is a consequence of different mechanisms, most likely also involving the pulp carbohydrates (Polcin, Rapson 1971; Lee et al. 1989; Luo et al. 1988; Holmbom et al. 1992; Grossmann, Ott 1994; Beyer et al. 1995; Fischer et al. 1995; Tylli et al. 1997).

Acetylation is an efficient way to retard the light-induced discoloration of both unbleached and bleached high-yield pulps (Manchester et al. 1960; Leary 1968; Lorås 1968; Ek et al. 1992; Paulsson et al. 1995; Hirashima, Sumimoto 1996; Paulsson et al. 1996; Itoh et al. 1997). The effect of acetylation on the heat-induced discoloration has, however, only briefly been examined. Lorås (1968) reported that vapor phase acetylation of unbleached and bleached (dithionite-, borohydride-, peracetic acid-, or hydrogen-peroxide-bleached) groundwood pulp improved the brightness stability upon exposure to heat (85°C) in a humid atmosphere. The stability was, however, not as pronounced as the photostability obtained by the same treatment. Acetylation has also been reported to increase the heat stability (both the physical and optical properties) of paper made from chemical pulp (Herdle, Griggs 1965; Ward 1973) as well as the dimensional stability of unbleached and bleached kraft saturating paper (Stamm, Beasley 1961). Furthermore, acetylation improved the mechanical properties of cellulose rag stock (Bletzinger 1943), kraft paper (Klinga, Back 1966), and paper made from high-yield pulps (Paulsson et al. 1994).

Aging under ambient conditions is a relatively slow process, and it is therefore necessary to use some form of accelerated testing to evaluate the heat (and light) stability of a paper (pulp) product. Today, several test methods for estimating the relative stability of paper are in use, e.g., dry heat treatments according to TAPPI Test Method T 453 pm -85 (105°C) and SCAN-C 32:78 (105°C), moist heat treatments according to TAPPI Test Method T544 pm-85 (90°C, 25% r.h.), ISO Standard 5630-3:1986(E) (80°C, 65% r.h.), and CPPA Standard E.4P (100°C, 100% r.h.). Several other test conditions have also been applied for the prediction of paper permanence in the literature (cf. Gurnagul et al. 1993). As in the case of light-induced aging, no general agreement on a standard heat-induced aging test has been established so far. However, the relative humidity under which samples are aged (in accelerated tests or during storage) influences the thermal stability. Several investigations have shown that increased humidity accelerates the heat-induced discoloration of both chemical and high-yield pulps (Tongren 1938; Giertz 1945; Gellerstedt et al. 1983; McLellan et al. 1990). It is therefore important that some moisture is present in the aging atmosphere chosen for the accelerated test (cf. Luner 1969).

Although accelerated tests give results that are difficult to relate to natural aging directly (cf. Arney, Jacobs 1980), several research groups have concluded that artificial aging is suitable for ranking the stability of a group of papers relative to each other (Rasch, Scribner

1933; Scribner 1938; Wilson et al. 1955; Luner 1969; Wilson, Parks 1980). Several studies have shown that aging of paper at 100°C for 72 hours is approximately equivalent to 25 years of natural aging (cf. Browning, Wink 1968). McLellan et al. (1990) compared ambient thermal brightness reversion (measured as Δk) with accelerated thermal aging and found that 24 hours at 105°C (0% r.h.) was equivalent to storing an unbleached (chelated) black spruce/balsam fir TMP in the dark for 390 days at 23°C (50% r.h.) and 270 days at 35°C (50% r.h.). The corresponding value for the hydrogen-peroxide-bleached TMP was 500 and 240 days, respectively. Care should, however, always be taken when accelerated tests are used to predict permanence in years because the precision of such a prediction is variable (Wilson, Parks 1980).

The research reported in this paper aims at obtaining knowledge about the heat-induced yellowing of different types of untreated and acetylated bleached high-yield pulps. The effect of two different accelerated aging methods (e.g., dry and moist heat) will also be discussed.

Experimental

Pulps and paper samples. Commercially produced dithionite(hydrosulfite)-bleached and hydrogen-peroxide-bleached spruce (*Picea abies*) TMP together with hydrogen-peroxide-bleached spruce (*Picea abies*) and aspen (*Populus tremuloides*) CTMP were used as received for the studies described in this paper. The pulps were obtained as dried samples. The high-brightness hardwood CTMP was manufactured employing hydrogen peroxide both as a chemical pretreatment and as a bleaching stage. Handsheets (60 $g \cdot m^{-2}$) were prepared according to TAPPI Test Method T 205 om-88. The paper sheets were then conditioned at 23°C and 50% r.h. according to TAPPI Test Method T 402 om-88 before further treatment.

Acetylation procedure. The handsheets [cut into strips (30 x 75 mm)] were acetylated (at 100°C or 110°C) according to the procedure described by Paulsson et al. (1994).

Analyses. The acetyl content was calculated from the amount of acetate liberated after saponification with sodium hydroxide as previously described in Paulsson et al. (1996). The acetyl content is given as a percentage of the dry weight of the paper.

Accelerated heat-induced aging. Heat-induced aging was performed at 105 ± 2°C according to TAPPI Test Method T 453 pm -85 (effect of dry heat) and at 80 ± 0.5°C and 65 ± 2% relative humidity according to ISO Standard 5630-3:1986(E) (effect of moist heat).

Optical measurements. TAPPI brightness and color changes according to the CIELAB color scale (L^*-, a^*-, b^*-values) were measured using a Technidyne Brightimeter (Model S-5) according to TAPPI Test Method T 452 om-92 and TAPPI Test Method T 524 om-94, respectively. The reflectance of a single sheet of paper (60 $g \cdot m^{-2}$) over a completely black, non-reflecting surface (over a hollow black body, reflectance <0.5%) and the reflectance over a stack of paper (high enough to inhibit any transparence of light) were recorded. The specific light scattering coefficient (s, at 457 nm) was then calculated using the Kubelka-Munk theory. The post color (PC) number (at 457 nm, according to Giertz 1945) was calculated for the acetylation treatment (PC_1) and for the heat-induced reversion (PC_2) (cf. Janson, Forsskåhl 1989). The sum of PC_1 and PC_2 represents the total effect of the treatment: $PC = PC_1 + PC_2$. The change in specific light-absorption coefficient (Δk, at 457 nm) during irradiation was calculated from the PC_2-value with the assumption of constant light scattering according to Johnson (1989).

Results and discussion

Four different types of commercially produced mechanical pulps, both oxidative (e.g., hydrogen peroxide) and reductive (dithionite) bleached, were examined. Three of the pulps were softwood-based (e.g., spruce, *Picea abies*); a dithionite-bleached thermomechanical pulp (TMP), a hydrogen-peroxide bleached TMP, and a hydrogen-peroxide-bleached chemithermomechanical pulp (CTMP). The fourth was a high-brightness, hydrogen-peroxide-bleached aspen (*Populus tremuloides*) CTMP (pretreated with hydrogen peroxide). It should, however, be pointed out that, although the pulps examined in this work represent a wide range of mechanical pulps, the pulp source used for the production of high-yield pulps influences the heat (and light) stability significantly (cf. Janson, Forsskåhl 1989; Johnson 1989; Lee et al. 1989).

The effect of heat on the optical properties of unacetylated high-yield pulps

Table 1 shows the effect of dry heat (105°C) and *Table 2* the effect of moist heat (80°C and 65% relative humidity) on the optical properties of the examined unacetylated and acetylated high-yield pulps. Comparison between the two aging conditions for the unacetylated pulps is given in *Figs. 1a* and *1b* where the brightness, as a function of aging time, is displayed. Generally, the dry heat aging condition was more detrimental to the brightness stability than was the moist aging condition, most likely due to a higher aging temperature in the former case. The decrease in brightness, caused by the heat treatment, was manifested as a decrease in lightness (L^*) and an increase in yellowness (b^*) for all of the unacetylated pulps. The a^*-value increased (which is equivalent to a more reddish hue of the paper) for all of the pulps except for the aspen CTMP aged under moist heat conditions where the a^*-value was unchanged.

As can be seen in *Figs. 1a-b*, the heat-induced yellowing is characterized by a rapid initial phase (large drop in brightness) followed by a slower less detrimental phase. This is the same behavior as previously reported for the light-induced discoloration process (cf. Lewis et al. 1945; Francis et al. 1991; Ek 1992; Paulsson et al. 1996; Paulsson, Ragauskas 1997a). The phases are, however, not so well-marked during heat-induced aging as during light-induced discoloration, especially not in the case of moist heat aging. The transition between the fast and slow phase seems to take place after about one day of heat-induced aging regardless of the conditions used.

The order of discoloration, among the untreated pulps, was determined to be dithionite-bleached spruce TMP≈hydrogen-peroxide-bleached spruce CTMP>hydrogen-peroxide-bleached spruce TMP>>hydrogen-peroxide-bleached aspen CTMP. The differences between the spruce pulps were, however, small. Interestingly, this is the same order of discoloration that previously was reported for the same pulps irradiated with various light sources (Paulsson, Ragauskas 1997b). The Δk-value was between 10.3 and 13.3 for the spruce pulps aged under dry conditions compared to 3.8-4.4 after moist heat aging, when the comparison was made after 6 days (144 hours) of reversion (see *Tables 1-2*). The corresponding values for the aspen CTMP were 7.1 and 1.0, respectively. It is evident that the high-brightness aspen CTMP is relatively less sensitive to heat-induced aging when moisture is present (only 1/7 of the reversion degree) than the bleached spruce pulps (about 1/3 of the reversion degree). Several investigations have shown that brightening with hydrogen peroxide or dithionite increases the thermal reversion of refiner mechanical pulp, groundwood pulp, and thermomechanical pulp (Jansen, Lorås 1968; Gellerstedt et al. 1983; Lee et al. 1989; McLellan et al. 1990; Holmbom et al. 1992). The reason for this is not clear. The formation

of new easily oxidizable lignin structures is one explanation (cf. light-induced reversion), although other possibilities exist.

The effect of heat on the optical properties of acetylated high-yield pulps

To see if acetylation altered the stability toward heat, the bleached pulps were acetylated to various degrees and then subjected to heat-induced aging. The results, summarized in *Tables 1* and *2* and in *Figs. 2* (dithionite-bleached spruce TMP), *3* (H_2O_2-bleached spruce TMP), *4* (H_2O_2-bleached spruce CTMP), and *5* (H_2O_2-bleached aspen CTMP), reveal that acetylation has a significant stabilizing effect both in dry and moist atmospheres. As can be seen in *Table 1*, the PC_2-number for the acetylated sheets (acetyl content of approximately 6%) aged under dry conditions stayed below 4.5 after an aging time as long as 144 hours. It is also evident that most of the stabilizing effect is reached after a rather low derivatization degree (e.g., acetyl contents in the range of 6-7%) regardless of the pulp type examined. The lightness (L^*) decreased and the yellowness (b^*) increased during aging as was the case for the untreated pulps.

The stability obtained in a humid atmosphere is also improved by acetylation, but the effect was not as pronounced (see b, *Figs. 2-5*). Noticeably, the brightness level of the acetylated aspen CTMP (acetyl content, 4.1%) was only marginally higher after reversion in a humid atmosphere due to the large brightness loss that occurred during acetylation (*Fig. 5*). Although most of the inhibiting effect is reached at a low acetyl content, increasing the derivatization degree above 6% strengthen the stabilizing effect of acetylation except in the case of H_2O_2-bleached spruce CTMP. There is, however, still changes in color after reversion, but the extent of the change was much smaller for the acetylated pulps.

The pronounced initial stabilization effect of acetylation suggests that acetylation eliminates or at least strongly retards the reaction pathways leading to colored chromophores, both during dry and moist heat aging conditions. Similarly, the improved long-term photostability, that has been reported for acetylated unbleached and hydrogen-peroxide-bleached high-yield pulps, is reached at rather low acetyl contents (cf. Paulsson et al. 1996). This suggests that heat- and light-induced reactions could involve very similar reaction schemes in the lignin part of the pulp constituents. The involvement of the carbohydrates can, however, not be excluded. A complete acetylation of all hydroxyl groups in softwood lignin corresponds to an acetyl content of about 7.5% calculated on wood [calculations are based on an average mass of a C_9 unit of 184 $g \cdot mol^{-1}$ (Rydholm 1965), lignin content of 29%, and a total number of hydroxyl groups of 1.45 per C_9 unit (Lundquist 1980), cf. Rowell 1982]. This means that wood components other than lignin are also acetylated, at least at higher derivatization degrees. [Complete acetylation of all accessible hydroxyl groups in spruce TMP corresponds to an acetyl content of approximately 40% (cf. Ek et al. 1992).]

In conclusion, although acetylation efficiently preserves a high brightness value in the paper, the structures formed during heat-induced aging still cause a yellow tint (an increase in b^*) in the acetylated paper. The discoloration is, however, much smaller than that for untreated handsheets aged under the same conditions; about 85-90% of the dry heat-induced yellowing (at 105°C) and more than 65% of the moist heat-induced yellowing (80°C, 65% r.h.) can be eliminated employing acetylation (in the interval examined) as an inhibiting treatment (see *Tables 1-2*).

Conclusions

This work demonstrated that the heat-induced discoloration of both oxidative and reductive bleached high-yield pulps can be reduced strongly by a low degree of acetylation regardless of the aging conditions used (e.g., 105° and 80°, 65% relative humidity). The facts that acetylation retarded most of the light-induced discoloration of both unbleached and bleached high-yield pulps (Paulsson et al. 1996) and the order of discoloration was approximately the same for the tested pulps both under light and heat exposure (cf. Paulsson, Ragauskas 1997b) support the hypothesis that light- and heat-induced yellowing involves the same type of reactions, preferably in the lignin part of the pulp constituents. However, because acetylation most likely also derivatizes some of the pulp carbohydrates (even at low acetylation degrees), the involvement of carbohydrate-generated chromophores on the heat-induced discoloration cannot completely be excluded. Experiments designed to clarify how the carbohydrates react during acetylation should be conducted.

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Figure captions

Fig. 1. The change in TAPPI brightness after heat-induced aging of different types of mechanical pulps. Abbreviations: a=105 °C; b=80 °C, 65% relative humidity. Legends: (❑), dithionite-bleached spruce TMP; (◊), hydrogen-peroxide-bleached spruce TMP; (○), hydrogen-peroxide-bleached spruce CTMP; (Δ), hydrogen-peroxide-bleached aspen CTMP.

Fig. 2. The change in TAPPI brightness after heat-induced aging of untreated (❑) and acetylated dithionite-bleached spruce TMP. Abbreviations as in Fig. 1. Legends (acetyl content): (◊), 6.2%; (○), 10.6%.

Fig. 3. The change in TAPPI brightness after heat-induced aging of untreated (❑) and acetylated hydrogen-peroxide-bleached spruce TMP. Abbreviations as in Fig. 1. Legends (acetyl content): (◊), 3.5%; (○), 6.7%.

Fig. 4. The change in TAPPI brightness after heat-induced aging of untreated (❑) and acetylated hydrogen-peroxide-bleached spruce CTMP. Abbreviations as in Fig. 1. Legends (acetyl content): (◊), 4.6%; (○), 9.4%.

Fig. 5. The change in TAPPI brightness after heat-induced aging of untreated (❑) and acetylated hydrogen-peroxide-bleached aspen CTMP. Abbreviations as in Fig. 1. Legends (acetyl content): (◊), 4.1%; (○), 6.0%; (Δ), 9.7%; (∇), 10.3%.

Table 1. Change in optical properties after heat-induced aging of untreated and acetylated high-yield pulps (TAPPI Test Method T 453 pm -85, effect of dry heat). Acetylation times (min) are given within parentheses.

Pulp	Acetyl content, % by mass	TAPPI brightnesss, %	L*	a*	b*	Heat-induced aging (dry heat, 105°C) 24 h TAPPI brightn., %	144 h TAPPI brightn., %	144 h L*	144 h a*	144 h b*	144 h PC_2-number[a]	144 h Δk[b]	144 h PC-number[c]
TMP (spruce), dithionite-bleached													
Control	1.4	65.7	92.1	-0.4	13.6	52.2	42.4	84.6	3.3	24.1	30.2	13.3	30.2
Acetylated (5)[d]	6.2	66.5	92.4	-0.5	13.2	64.1	60.6	90.5	-0.4	15.3	4.4		3.9
(15)[d]	10.6	67.5	92.8	-0.6	13.0	65.4	62.6	91.3	-0.7	14.8	3.3		2.2
TMP (spruce), H_2O_2-bleached													
Control	0.2	75.0	95.0	-1.7	10.7	64.0	51.0	88.8	1.1	21.8	19.4	10.3	19.4
Acetylated (5)[d]	3.5	73.7	94.9	-1.8	11.6	69.8	61.5	91.8	-0.8	16.8	7.4		7.9
(15)[d]	6.7	72.7	94.9	-1.9	12.4	70.8	67.9	93.4	-1.9	13.9	2.5		3.4
CTMP (spruce), H_2O_2-bleached													
Control	0.5	78.2	95.4	-1.9	8.8	60.6	46.7	86.9	2.1	23.2	27.3	13.2	27.3
Acetylated (5)[d]	4.6	76.3	95.2	-2.0	10.0	71.1	64.0	92.3	-0.7	15.2	6.5		7.1
(15)[d]	9.4	75.6	95.1	-2.1	10.4	73.2	69.0	93.5	-1.5	13.1	3.4		3.9
CTMP (aspen), H_2O_2-bleached													
Control	0.6	84.3	95.8	-1.0	4.6	70.9	53.7	90.2	-0.1	21.4	18.5	7.1	18.5
Acetylated (5)[d]	4.1	81.0	95.3	-1.4	6.4	76.6	71.0	94.1	-2.0	12.3	3.7		4.5
(10)[d]	6.0	78.6	94.9	-1.3	7.6	75.9	72.8	94.2	-1.8	10.9	2.2		3.6
(10)[e]	9.7	74.6	93.7	-1.1	8.8	71.9	68.7	93.4	-1.6	13.1	2.7		5.6
(25)[d]	10.3	73.7	93.7	-1.1	9.3	72.1	69.2	93.3	-1.4	12.5	2.2		5.4

[a]The post-color (PC_2) number at 457 nm (due to irradiation) was calculated according to Giertz (1945).

[b]The change in light absorption (Δk) was calculated from the PC_2-value with the assumption of constant light scattering according to Johnson (1989).

[c]The post-color (PC) number at 457 nm [due to acetylation (PC_1) and heat-induced aging (PC_2)] was calculated according to Giertz (1945).

[d]Acetylation temperature, 100°C.

[e]Acetylation temperature, 110°C.

Table 2. Change in optical properties after heat-induced aging of untreated and acetylated high-yield pulps (ISO Standard 5630-3:1986(E), effect of moist heat). The optical properties before the moist heat treatment are given in Table 1. Acetylation times (min) are given within parentheses.

Pulp		Acetyl content, % by mass	Heat-induced aging (moist heat, 80°C and 65% r.h.) 24 h TAPPI brightn., %	144 h TAPPI brightn., %	L*	a*	b*	PC_2-number[a]	Δk[b]	PC-number[c]
TMP (spruce), dithionite-bleached										
Control		1.4	60.2	54.7	89.0	1.1	16.5	9.9	4.4	9.9
Acetylated	(5)[d]	6.2	64.9	62.3	91.2	-0.2	14.9	3.0		2.5
	(15)[d]	10.6	66.1	64.8	91.6	-0.6	13.2	1.8		0.6
TMP (spruce), H_2O_2-bleached										
Control		0.2	69.1	62.4	91.9	-0.6	16.0	7.1	3.8	7.1
Acetylated	(5)[d]	3.5	71.5	67.9	93.3	-1.3	13.6	2.9		3.4
	(15)[d]	6.7	72.1	70.4	93.9	-1.7	12.6	1.1		2.1
CTMP (spruce), H_2O_2-bleached										
Control		0.5	69.1	62.0	91.6	-0.2	15.9	8.6	4.2	8.6
Acetylated	(5)[d]	4.6	73.4	69.3	93.7	-1.2	13.2	3.2		3.8
	(15)[d]	9.4	73.1	69.0	93.2	-1.2	12.6	3.0		3.9
CTMP (aspen), H_2O_2-bleached										
Control		0.6	79.7	74.9	94.5	-1.0	9.6	2.7	1.0	2.7
Acetylated	(5)[d]	4.1	78.8	76.2	94.9	-1.4	9.4	1.5		2.3
	(10)[e]	9.7	74.7	73.0	94.2	-1.5	10.8	0.7		3.5
	(25)[d]	10.3	74.1	72.7	94.2	-1.4	11.0	0.4		3.7

[a]The post-color (PC_2) number at 457 nm (due to irradiation) was calculated according to Giertz (1945).

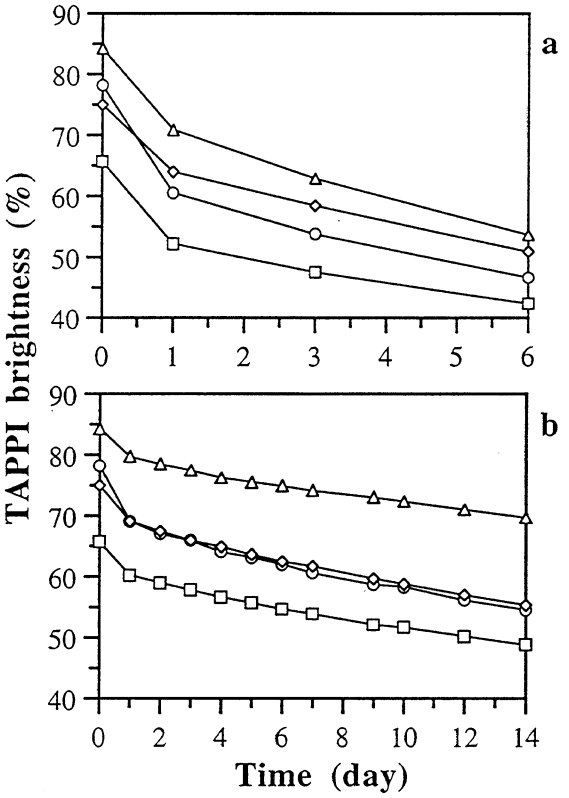
[b]The change in light absorption (Δk) was calculated from the PC_2-value with the assumption of constant light scattering according to Johnson (1989).

[c]The post-color (PC) number at 457 nm [due to acetylation (PC_1) and heat-induced aging (PC_2)] was calculated according to Giertz (1945).

[d]Acetylation temperature, 100°C.

[e]Acetylation temperature, 110°C.

Figure 1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70
60
50
40
0
1
2
3
4
5
6
a
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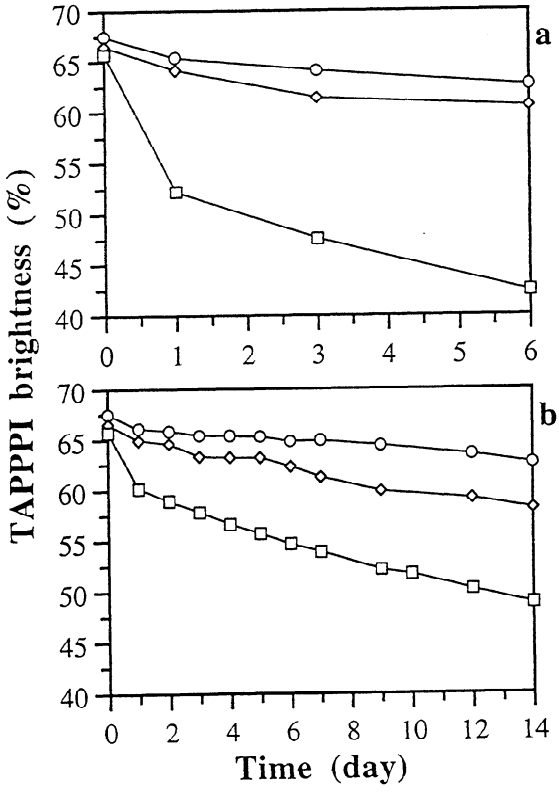
80
70
60
50
40
0
2
4
6
8
10
12
14
b
Time (day)

Figure 2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4
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6
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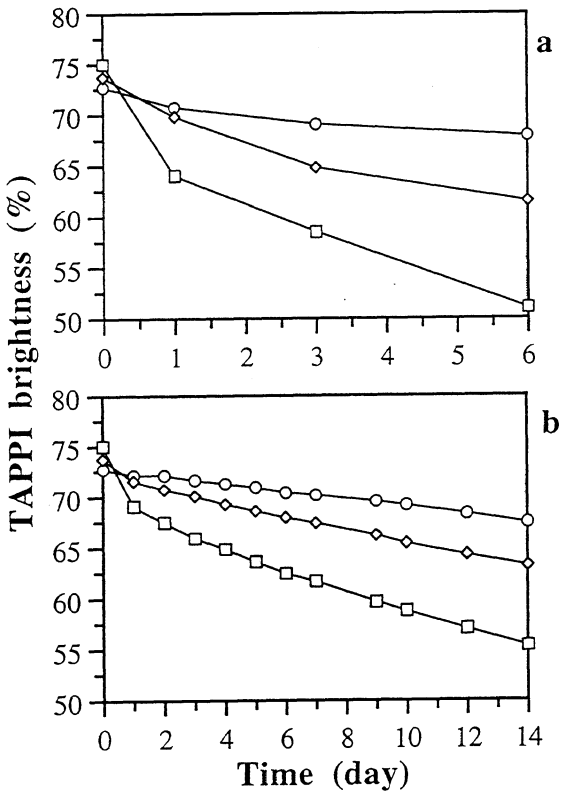
60
55
50
45
40
0
2
4
6
8
10
12
14
b
Time (day)

Figure 3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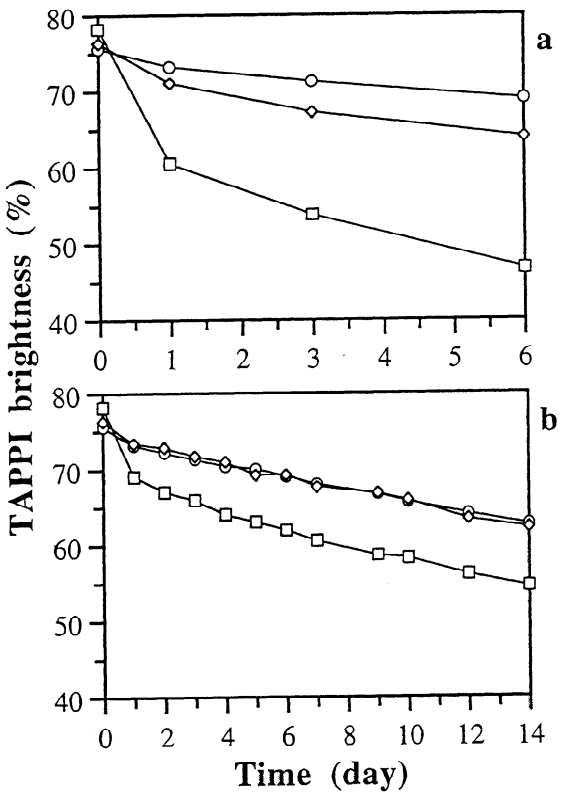
70
65
60
55
50
0
1
2
3
4
5
6
a
80
75
70
65
60
55
50
0
2
4
6
8
10
12
14
b
Time (day)

Figure 4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3
4
5
6
a
80
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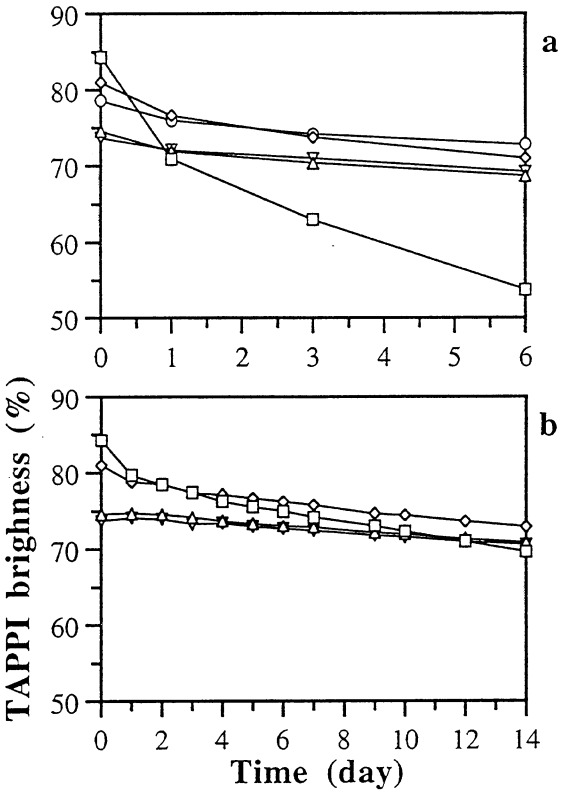
40
0
2
4
6
8
10
12
14
b
TAPPI brightness (%)
Time (day)

Figure 5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0
1
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3
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b
0
2
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6
8
10
12
14
TAPPI brighness (%)
Time (day)